PATENT SPECIFICATION (11) 1395065

(21) Application No. 30253/72 (22) Filed 28 June 1972

(61) Patent of Addition to No. 1288583 dated 17 Nov. 1969

(31) Convention Application No. 5329/71 (32) Filed 28 June 1971 in

(33) Australia (AU)

(44) Complete Specification published 21 May 1975

(51) INT CL² C08J 9/28 C09D 3/74

(52) Index at acceptance

C3C 136 180 181 182 183 301 358 369 372 413 414 452 455 520 521

C3P 4C13B 4C14A 4C8B 4C9 4D3B1 4K8 8C13B 8C14A 8C8B 8C9 8D2A 8K4 E2

(19)

(54) MATTE PAINTS

(71) We, DULUX AUSTRALIA LIMITED (formerly Balm Paints Limited), of 1 Nicholson Street, Melbourne, Victoria, Australia, a Company organised and existing under the laws of the State of Victoria, Commonwealth of Australia,

do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to matte paints and paint films.

It is an art-recognised practice to make matte paints by incorporating in a suitable film-forming vehicle (or medium) relatively large volume concentrations of pigment. When a film of the paint dries the pigment disrupts the exposed surface thereof, scattering light reflected from the surface and producing a visual effect which, according to the degree of scattering, is referred to by terms such as satin, semi-gloss, eggshell and matte. The particular paints referred to herein as matte paints are those which exhibit a high degree of light scattering. The dried films when tested by the method of the American Society for Testing and Materials method D-523-62T using an 85° gloss head and a Gardner Photo-electric automatic Gloss Meter ("Gardner" is a Registered Trade Mark), have a gloss reading of less than 15 units.

The composition of the pigment used to produce matte paints in this way is not critical but because of the high cost of prime pigments, e.g. titanium dioxide, zinc oxide and antimony oxide, it is usual to limit the concentration of prime pigment to the minimum amount necessary to achieve an acceptable opaque film and to use relatively large concentrations of extender pigment, e.g. talc, clay, barytes and silica, to give the desired gloss level.

Although useful matte paints have been produced by this technique they are prone to certain defects such as excessive marring, dirt collection, rub-up and sheeriness or low opacity; associated with their high pigment loadings. For example, the use of relatively coarse extenders will usually result in hard, matte films but of relatively poor opacity. The use of very fine extenders, often of sub-micron dimensions, has been proposed to provide good opacity with low gloss, but it is difficult to produce matte paints with satisfactory scrub resistance and re-coat properties by this method, the compromise which must be reached favouring somewhat higher gloss levels than those described above.

In British Patent No. 1,288,583 it was disclosed that certain suitably sized polymeric granules can be used as matting agents for paint and due to their vesiculated structure they also confer opacity on the paint film. Thus, it becomes possible by the use of these granules to produce matte paint films without the attendant disadvantage of loss of opacity. Paint films of this type also exhibit a high resistance to abrasion and dirt collection, even at very low gloss levels.

By vesiculated polymer granules we mean granules of polymer, which should preferably be spheroidal, and which contain vesicles, the walls of the vesicles being provided by solid polymer. Each granule comprises a plurality of vesicles; that is it is not balloon-like, nor does it have the open-pored cellular structure of a sponge. The surface of the granules should be essentially non-porous with respect to the medium in which they are to be incorporated. That is, while some random minor occurrence of imperfect vesicles due to the absence of a portion of the outer surface wall of the granules can be tolerated, this should be avoided as far as possible to prevent granules imbibing medium and thus reducing their effective vesicle volume in a dry paint film. Essential requirements in these granules are that the ratio of granule diameter to mean vesicle diameter is at least 5 to 1, the volume of

vesicles is 5—95% of the total volume of the granules, the maximum diameter of the vesicles is less than 20 micron.

Optionally, the polymer of the granules and/or the vesicles may contain insoluble particulate matter, especially pigment particles, to further enhance the opacifying effect of the granules.

In the above-mentioned patent specification it was disclosed that granules of this type, in which the vesicles occupied 5—95% of the granule volume could be used with advantage to prepare opaque paints comprising (a) film-forming vehicle, (b) pigment dispersed therein to a pigment volume of 0—85% of the solids volume of (a) plus (b), and (c) insoluble vesiculated polymer granules dispersed in the vehicle at a volume concentration of 5—95% of the total solids volume concentration of the composition.

By the selection of suitably sized granules, the compositions so-produced could be made to form matte paint films of unusually uniform visual appearance. For the best results, it was disclosed that the granules should have a volume average diameter of from 5 to 35 micron and a mean diameter of 1—50 micron.

Within this broad field of matte paint compositions disclosed hitherto, we have now discovered that for optimum results further limitations must be placed on the chosen formulations.

Bearing in mind that the above-described vesiculated granules are somewhat similar in size and function to the extender pigments hitherto used as matting agents in flat paints, it has been proposed that they should be considered, in deriving satisfacory paint formulations, as "extender pigment" and that the existing criteria which limit paint formulations would still hold if this assumption was made. Surprisingly, we have now discovered that this is not so and we now disclose preferred highly opaque matte paints comprising vesiculated granules in which the proportions of ingredients are defined by new criteria which admit of compositions of satisfactory opacity containing much higher granule concentrations than would have been predicted by analogy with known paint compositions utilising conventional flatting agents.

In order to more clearly distinguish our preferred matte paint compositions we have found it desirable to consider the granules and the balance of the composition separately and to define the paint in terms of the composition of a dried film formed therefrom. The concept of relating paint composition to the dry film is in itself not novel, since it is implicit in, for example, applying the parameter of critical pigment volume concentration to paint formulations. An experienced formulator can, of course, relate the composition of the dry film to that of the parent liquid paint, using his knowledge of the art. The critical pigment volume concentration is a well-known parameter at which there is a marked transition in the mechanical properties of paint films and is defined, for example, in "Industrial and Engineering Chemistry" *41*, 17, 1470 (1949), and is related to the relative volume concentration of pigment and film-forming medium often referred to as the binder, in the dry film. The connection between the binder in a dried paint film and the composition of the liquid paint composition from which that film is derived is well understood in the art. In a dried paint film, it is the film-forming components derived from the film-forming vehicle which constitute the binder.

The dried film of the type to which this invention relates consists of a polymeric film-forming binder, which has pigment dispersed therein, in which is embedded the vesiculated polymer granules. We find it convenient to refer to all of the components other than the vesiculated granules as the "matrix", in which the granules are embedded.

Two parameters can then be applied to the composition of the paint film, the pigment volume concentration in the matrix (M.P.V.C.) and the granule volume concentration (G.V.C.) in the dry film. These parameters are defined as follows:

$$\text{M.P.V.C.} = \frac{\text{total volume of pigment in the matrix}}{\text{total volume of matrix}} \times 100\%$$

$$\text{G.V.C.} = \frac{\text{total volume of granules in the dry film}}{\text{total volume of the dry film}} \times 100\%.$$

According to the present invention we provide a matte paint composition which provides a dried paint film being a gloss as hereindefined of less than 15 units, the composition comprising a pigment dispersed in a polymeric film forming vehicle to a pigment volume concentration in the matrix as herein defined of 5—78% and vesiculated polymer granules dispersed therein to a granule volume concentration as herein defined of 25—60%, the vesiculated polymer granules having a mean diameter of 1—50 micron and a volume average diameter of 5—35 micron.

We have discovered that in order to

achieve the best results in formulating matte paints of good opacity, the G.V.C. should lie within the range of 25 to 60 and preferably 35 to 50%. At lower granule concentrations, sheeriness and non-uniformity of appearance of the paint becomes increasingly evident, while at higher granule concentrations there is no useful increase in flatting but the film becomes progressively mechanically weaker. This visual effect appears to be largely independent of the pigment content of the matrix.

Within the above G.V.C. limits, a second controlling factor is the pigment volume concentration in the matrix and this should be in the range 5—78% but we have found that the best matte paint films of high opacity and film integrity lie within the limits of 5—35% M.P.V.C. Such films have a low porosity and good re-coating properties.

The present invention also provides dry matte paint films in which the film comprises 7—30% by volume of vesicles the vesiculated granules have a vesicle volume of 20—60%.

For some purposes, for example in ceiling paints, some scrub-resistance can be sacrificed to achieve very low gloss. We have now found that paints of this type with gloss levels lower than 10 units (85° gloss head) can be prepared by working at M.P.V.C. values of up to 78%. In partiuclar, when the M.P.V.C. exceeds the critical M.P.V.C. (the 'conventional' critical pigment volume concentration with reference to the matrix composition) the paint films have outstanding hiding power. At lower values of M.P.V.C. the opacity is significantly reduced and at higher values of M.P.V.C. the films are usually too low in scrub resistance to be useful. The useful upper limit depends to a degree on the nature of the particular matrix bearing in mind that acceptable scrub resistance is a subjective judgement.

In general, we have found that to ensure optimum opacity and satisfactory mechanical strength in the dry paint film, the granules should preferably comprise 20—60% by volume of vesicles and relating this to our preferred G.V.C. concentration this means that the dry film will preferably contain from 7 to 30% by volume of vesicles provided by the granules.

The paints are readily prepared by stirring granules into the paint vehicle, which consists of the matrix in solution or disperse form in a suitable volatile liquid.

The invention is illustrated by the following Examples in which all parts are by weight, the paints having a gloss level of less than 15 units of the ratio of granule diameter to mean vesicle diameter being at least 5 to 1:

Example 1

Effect of granule volume concentration on the properties of matte paints comprising vesiculated polymer granules.

A series of paints was prepared from the following materials:

Granules—cross-linked polyester resin vesiculated granules of mean diameter in the range 1—50 micron, 15 micron volume average diameter, less than 30 micron maximum diameter 0.7 micron mean vesicle diameter and 45% vesicle volume. The granules comprised 20% by weight of rutile titanium dioxide pigment which was distributed throughout the vesicles. The granules had an essentially continuous, non-porous polymer surface.

Latex—A commercially vinyl acetate/acrylic copolymer aqueous latex of 55% by weight total solids.

The paint were prepared at a range of granule volume concentrations as shown in the accompanying table and at a constant M.P.V.C. of 30% using rutile titanium dioxide as the sole pigment in the latex.

The titanium dioxide was dispersed in a 15.7% by weight slurry of the appropriate granules in water using a conventional sand mill and in the presence of 0.5% by weight of sodium hexametaphosphate, based on the weight of pigment. The latex was then added with slow stirring and the viscosity adjusted as required to give a suitable rheology for brush application by the addition of extra water.

The paints were tested for opacity by the method described below and for re-coating properties by practical brushing trials on hardboard sheets. Uniformity of appearance of the dry films, noting in particular any irregularities of gloss level, was judged visually from the dry paint films. The scrub-resistance was measured by the American Society for Testing and Materials method D 2486-69T.

The paint samples were brushed out onto Morest Charts at a spreading rate of about 600 sq.ft. per gallon and allowed to dry in air. The opacities of the dry films were compared with a set of standards which had been given an arbitrary rating of 0 (no capacity) to 16 (complete obliteration), in approximately linear increments of opacity.

Paint No.	% Gran. vol. conc. (G.V.C.)	Uniformity appear	Opacity	Recoat Props	Scrub Resist.*
1	0	poor. Very uneven	8	Excellent	800
2	20	Sheery	8	„	650
3	40	Good	9	„	400
4	50	Excellent	10—11	Good	250
5	60	„	9	Fair	150
6	70	„	8	Poor	50

* Scrub cycles to film failure.

The results show that a G.V.C. below and above the range of 25 to 60% the paints were of unacceptable appearance and mechanical properties respectively. Compositions within out preferred G.V.C. range of 35 to 50% had good mechanical properties and a superior combination of appearance and opacity to the other paints in the series.

Example 2

Effect of matrix pigment volume concentration on the properties of matte paints comprising vesiculated polymer granules.

A similar series of paints to that of Example 1 was prepared from the same titanium dioxide pigment granules and latex. The paints were, however, prepared at a constant granule volume concentration of 45% and the matrix pigment volume concentration (MPVC) was varied by adjusting the proportion of titanium dioxide dispersed therein. Testing of the paints was carried out as in Example 1 with the following results:

Paint No.	% M.P.V.C.	Opacity	Scrub Res.	Recoat Resist.
1	3	3	500	Excellent
2	10	6	400	„
3	20	7	400	„
4	30	9—10	350	„
5	40	15	200	Fair
6	50	15	100	Poor
7	80	20	10	Very Poor

The critical pigment volume concentration of the matrix was determined to be about 35%, so that paints 5, 6 and 7 exceed this critical value. Hence they represent compositions in which a balance between film integrity and opacity has been struck in favour of high opacity. Paint 1, which lies below our preferred M.P.V.C. range, had very poor opacity, while paint 7, which exceeded out upper M.P.V.C. limit for high opacity films, showed unacceptably poor film integrity.

Example 3

Effect of some granule variables on the opacity of dry paint films in which the granules are incorporated.

Spheroidal granules of an unsaturated polyester resin cross-linked by reactor with styrene monomer were prepared as a 23% by weight slurry in water. The granules had a volume average diameter of 13 micron (all granules were less than about 32 micron diameter), a vesicle volume of 50% and comprises vesicles of 0.5 micron mean diameter containing approximately 20% by volume of titanium dioxide pigment. The granules had an essentially non-porous outer surface and as a check on their vesicle volume, estimated initially from an electron microscope examination, this was recalculated in the following manner.

To 34.44 parts of an acrylic latex of 46.5% by weight solids was added with mixing 5.22 parts of the slurry of granules. A thick film was built up on a glass plate by depositing with a doctor blade and drying on it successive layers of the above mixture. The dried film was removed from the glass and its density measured using a specific gravity bottle, in which the film was immersed in water. The results were as follows:

weight of film	0.6146 gm.
volume of film	0.556 ml.
Specific gravity of solid acrylic film-forming polymer	1,124

The density of the granules was calculated from these figures to be 0.91 gm per cm^3, from which their calculated vesicle volume is about 50%.

The slurry of granules was used to prepare a paint by the general method of

Example 1 using the following ingredients:

	parts
granules slurry (as above)	200.0
titanium dioxide pigment	32.0
sodium hexametaphosphate	0.1
hydroxy ethyl cellulose	0.6
latex (as example 1)	100.0

The paint so-prepared was tested by the methods used in example 1, with the following results:

Opacity	9
scrub resistance	450
recoat properties	excellent
resistance to polishing (rubbing of dry film)	good

The volume of vesicles in the dry film was estimated by the above-described density method, making due allowance for the presence of pigment particles in the vesicles (which affect the granule density but not the vesicle volume) and this was found to be about 20%, which is consistent with a fully bound paint film with a vesiculated granule content as prepared. The M.P.V.C. and G.V.C. were within the ranges required by the invention.

By way of comparison, a similar paint film was prepared in which the above granules were replaced on an equal volume basis by granules of similar size but with a vesicle volume of 75%. The measured vesicle volume of a dry film of this paint, which had good opacity was about 35%. The resistance of the film to polishing was, however, markedly inferior to that of the film having the lower measured vesicle volume of 20%.

In a furter comparative test, another paint was prepared replacing the vesiculated granules containing 20% by volume of titanium dioxide in the vesicles with granules similar to other respects but in which the titanium dioxide was omitted from the vesicles. A corresponding weight of titanium dioxide was, however, added to the 32.0 parts of that pigment used in preparing the paint. Thus the two paints had equal contents of titanium dioxide and differed primarily in that in one case the pigment was distributed between the matrix and the vesicles of the granules, whereas in the other all of the pigment was present in the matrix. The opacity of a dry film of the latter paint was estimated to be 7, which illustrates the gain in opacity by utilising some of the pigment as an inclusion in the granule vesicles.

WHAT WE CLAIM IS:—

1. A matte paint composition which provides a dried paint film having a gloss as hereinbefore defined of less than 15 units, the composition comprising pigment dispersed in a polymeric film-forming vehicle to a pigment volume concentration in the matrix as hereinbefore defined of 5—78% and vesiculated polymer granules dispersed therein to a granule volume concentration as hereinbefore defined of 25—60%, the vesiculated polymer granules having a mean diameter of 1—50 micron and a volume average diameter of 5—35 micron.

2. A matte paint composition according to claim 1 in which the polymer of the granules and/or the vesicles contain pigment.

3. A matte paint composition according to claim 1 or claim 2 in which the granule volume concentration is 35—50%.

4. A matte paint composition according to any one of claims 1—3 in which the pigment volume concentration in the matrix is 5—35%.

5. A matte paint composition according to any one of claims 1—3 in which the composition provides a dried paint film having a gloss of less than 10 units and the pigment volume concentration in the matrix exceeds the critical pigment volume concentration in the matrix but is less than 78%.

6. A dry matte paint film provided by a composition according to claim 1 or claim 2 in which the dry film comprises 7—30% by volume of vesicles and the vesiculated granules have a vesicle volume of 20—60%.

7. A matte paint composition according to claim 1 and substantially as hereinabove described with reference to any one of the Examples.

D. VINCENT,
Agent for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1975.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.